CONTRIBUTION TO THE KINETICS OF CHROME TANNING. PART I. THE EFFECT OF THE FLOAT RATIO*

J. C. DE WIJS

Institute for Leather and Shoe Research TNO
Waalwijk, Holland

ABSTRACT

A study has been made on the influence that the float ratio has on the rate of chrome retention by hide powder tanned in chromium sulfate liquors. Depending on the conditions of tanning, an increase of the float ratio can result in an increased, a decreased, or even an increased followed by a decreased, speed of the reaction and chrome fixation. In addition to the kinetic aspect of the tanning reaction, these effects are explained by considering also the changes in the properties of the chrome liquors and of the pH level of tanning as a consequence of a variation in the tanning conditions.

INTRODUCTION

Like nearly all chemical reactions, chrome tanning is a rate process and therefore governed by kinetic principles. Tanning reactions are, however, of a complex nature, since many chemical and physical factors are involved. It can be expected that these factors also affect the rate of chromium retention by the hide substance.

Much work has been done in the past to elucidate the effect of such factors on the uptake of chromium, but information on how they influence the rate of the chrome-tanning process proper is limited (1, 2). As chrome tanning requires a number of hours, investigations on the kinetics of chrome tannage can be of benefit in a study of the possibility of reducing the time of tanning. Decreasing this time would make the process more economical and could lead to greater mechanization.

From these viewpoints, a detailed study has been made on the influence of different variables in chrome tanning on the rate of chromium retention by hide powder, in order to obtain more fundamental information on how the speed of the tanning process can essentially be regulated. The concentration and the basicity of the chrome liquor, the ratio of the volume of the tanning solution to

*This research has been financed in part by a grant made by the United States Department of Agriculture under P.L. 480.

the weight of collagen, the kind and concentration of inorganic or organic salts in the chrome liquor, and the temperature of tanning are some of the factors that were studied. In practice, several of these factors occur simultaneously. For this reason, the combined effect of some of these factors on the rate of chrome tanning was partly taken into consideration in the course of these investigations. This first paper deals with the effect of float ratio. Practical chrome tanning is carried out with very divergent ratios of the volume of the tanning liquor to pelt weight (float ratio). In paddle tanning a large float ratio is used, while in drum tanning this ratio is medium or low.

In the literature, very little basic information is found on the influence of this factor on the uptake of chromium by hide substance. According to Otto (3), the fixation of chromium by neutral pelt from a 33 percent basic chromium chloride liquor of 0.12 mole Cr_2O_3/1. decreases with increasing float ratio (eight hours of tanning). The same trend was found by Gustavson (4, 5) for tanning times up to 24 hours, but for longer periods of tanning the float ratio of such tanning liquors seems to have no effect on chromium uptake. When tanning is done, however, with chromium sulfate liquors of 35 and 57 percent basicity and 0.13 mole Cr_2O_3/1., this author found that, for both short and long duration of tannage, chromium uptake by pelt is independent of the float ratio.

The present paper describes the effect of float ratio on the rate of chrome retention by hide powder tanned in chromium sulfate liquors for two different conditions, *viz.*, at a constant initial percentage of chromium to collagen, and at a constant initial chromium concentration of the tanning solution. In both cases, the influence of the basicity of the chrome liquor was also studied to some extent.

EXPERIMENTAL

Standard chrome liquors

Chrome liquors (Series A) with basicities of 32.0 and 40.2 percent and free from neutral salts were prepared from hexaquo-chromium sulfate. The required amounts of this salt were dissolved in three times their weight of water and boiled for one hour. On the next day a suspension of the calculated amount of calcium hydroxide was added carefully to the heated chrome solutions, and the solutions were boiled for another hour, cooled, and allowed to stand for some days. Then they were filtered to remove calcium sulfate and diluted to 0.2 mole Cr_2O_3 per liter.

A second series (Series B) of chrome liquors were obtained from a commercial, dry, 50 percent basic chrome-tanning material, containing 36 percent Cr_2O_3 and three percent Na_2SO_4. Calculated amounts of this product were suffused with about 2.5 times their weight of boiling water, with stirring. After cooling, concentrated sulfuric acid was added in order to obtain chrome liquors with basicities of about 32.40 and 47 percent, respectively, and the solutions were diluted

to 0.5 mole Cr_2O_3 per liter. They contain the same low amount of sodium sulfate, so that the effect of a different neutral salt content at various basicities on chrome retention is eliminated. All chrome liquors were aged for at least two months at room temperature before use.

Tanning procedures

Hide powder was used in these studies, in order to work with a homogeneous material and to eliminate to a fair extent the influence of diffusion on the rate of chrome fixation proper, a factor that would occur in tanning hide pieces.

Portions of 2.5 grams hide powder were soaked overnight in bottles with water at room temperature. Then the required volume of water was added, depending on the float ratio and on the initial chrome concentration of the tanning solution, and the bottles were placed for half an hour in a thermostat at 20°C. ± 0.1°C. Thereupon the calculated volume of the standard chrome liquor of the same temperature was added. Tanning proceeded with constant shaking for one to eight hours. After the end of a predetermined time, the chrome liquor was suctioned off into a glass vessel for pH measurement, a determination which was made immediately. The tanned hide powders were washed by suspending them in four changes of 100 ml. of distilled water, stirred, and filtered again. They were dried at 110°C.

Chromium oxide was determined in accordance with the fusion method of IUC/8 (6), and total nitrogen by semimicro Kjeldahl techniques. All results are expressed as percent Cr_2O_3 on hide substance.

1. THE EFFECT ON CHROME RETENTION OF FLOAT RATIO WITH CONSTANT INITIAL PERCENTAGE OF CHROMIUM TO COLLAGEN

For these experiments, chrome liquors of Series A were used. Tanning was performed with 2.5 grams hide powder in a total volume of 50, 100, 200, or 400 ml. chrome solutions with an initial amount of 34 percent Cr_2O_3 on collagen. The float ratios therefore varied from 20:1 to 160:1.

Results

The uptake of chromium by hide powder tanned in these chrome liquors for various times is shown in Figure 1. The rate of reaction and the retention of chromium decrease with increasing volume of the tanning liquor, irrespective of the basicity. The pH level of tanning increases with increasing float ratio (Figure 2). For each experimental condition there is a sharp rise in the pH value of the spent chrome solutions during the first period of tanning, followed by a slower and continuous decrease when tanning proceeds.

Discussion

An increase of the volume of a tanning solution with a constant initial ratio of chromium to collagen means that the initial chromium concentration (moles

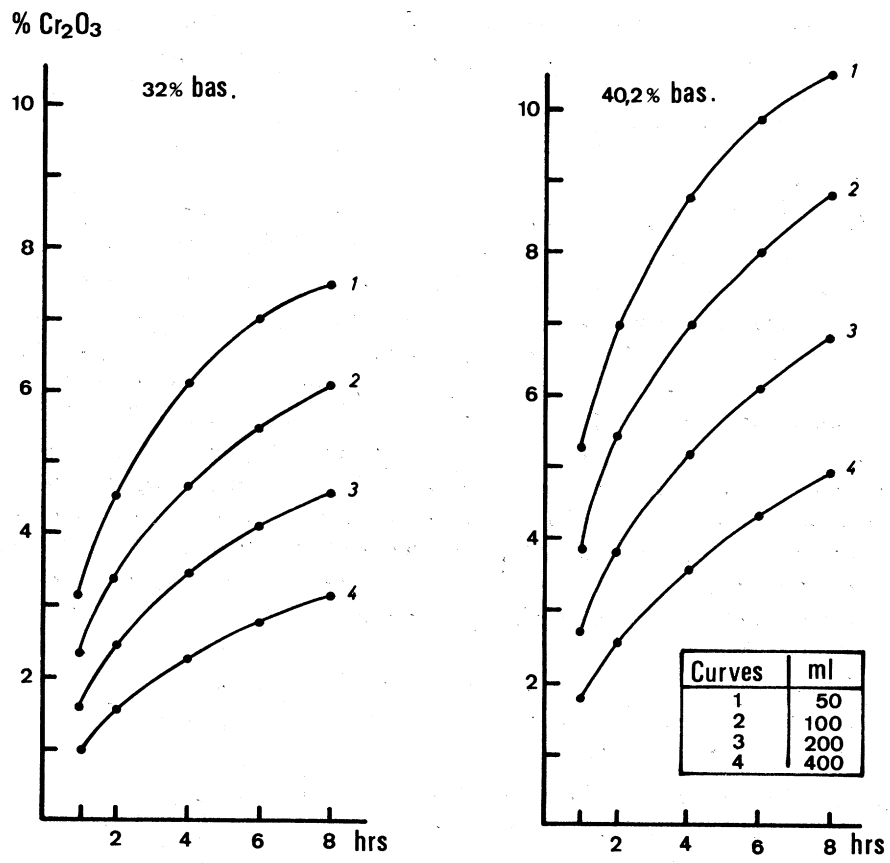

FIGURE 1.—Chrome retention by hide powder. Influence of the volume of chrome liquors having constant initial ratio of 34 percent Cr_2O_3 to collagen and different basicities.

Cr_2O_3/l.) decreases at the same time. Therefore, according to kinetic laws, the rate of reaction diminishes and the uptake of chromium by collagen also decreases as the float ratio increases.

A lower initial chrome concentration, however, involves changes in the composition of the chromium complexes due to hydrolysis, by which more complexly bound hydroxy groups are formed. This results in chromium complexes of higher basicity and therefore in a rise of their electrochemical equivalent weight (lower positive charge per chromium atom). This increase of the complex basicity stimulates the olation reactions, which will give larger chromium complexes with more hydroxy groups per complex available for hydrogen bonding between these groups and collagen. A combination of these effects leads to a greater affinity of the chromium complexes for collagen, and so to an increased reaction velocity and to a higher fixation of chromium. In addition, these effects are supported by higher

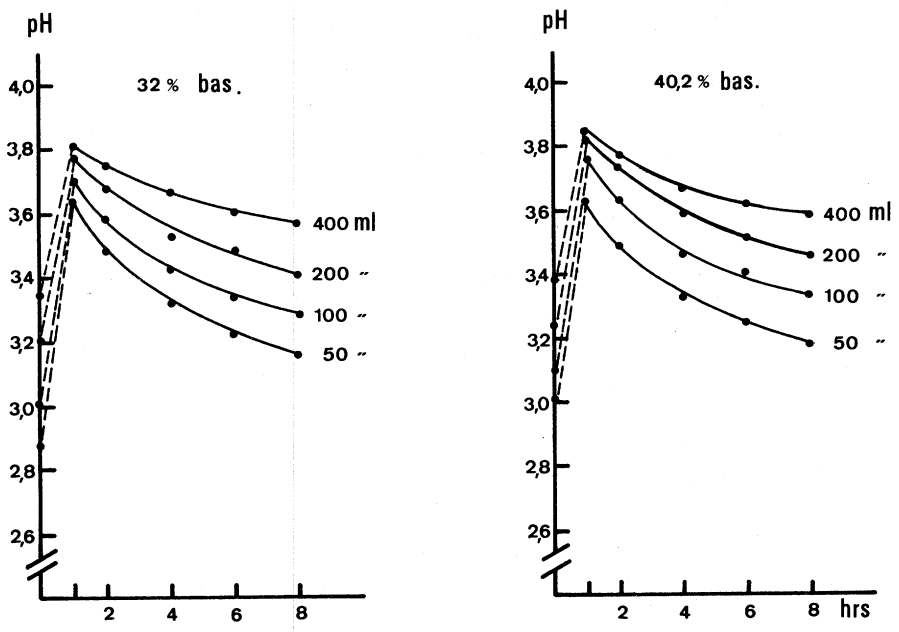

FIGURE 2.—pH values of spent chrome-tanning solutions having constant initial ratio of 34 percent Cr_2O_3 to collagen and different basicities.

pH levels of tanning due to dilution of the chrome solution, by which the ionization of the carboxyl groups of collagen is promoted. The experimental results show that the first-mentioned effect of increasing the volume of tanning, *viz.*, lower initial chromium concentration, dominates the influences of changes in the composition of the chromium complexes and of the pH level of tanning, because the rate of reaction, as well as the amount of chromium retained by collagen, decreases as the float ratio increases.

When hide powder is tanned in a chrome liquor, acid is removed from the solution as it is fixed by the reactive groups of collagen. Hence the pH value of the tanning solution increases in the first instance. Owing to the removal of acid, the hydrolysis equilibrium in the chrome solution is disturbed. To restore this equilibrium, chromium complexes in the solution will hydrolyze, a result which leads to an increase of the hydrogen ion concentration of the tanning liquor. This accounts for the continuous fall in the pH values of the spent chrome liquors during tanning.

2. THE COMBINED EFFECT ON CHROME RETENTION OF CONCENTRATION, FLOAT RATIO, AND RATIO OF CHROMIUM TO COLLAGEN

An increase of the ratio of chromium to collagen can be achieved either by increasing the concentration of the chrome liquor at constant volume or by increasing the volume of the tanning solution. The graphs of Figure 3 show how

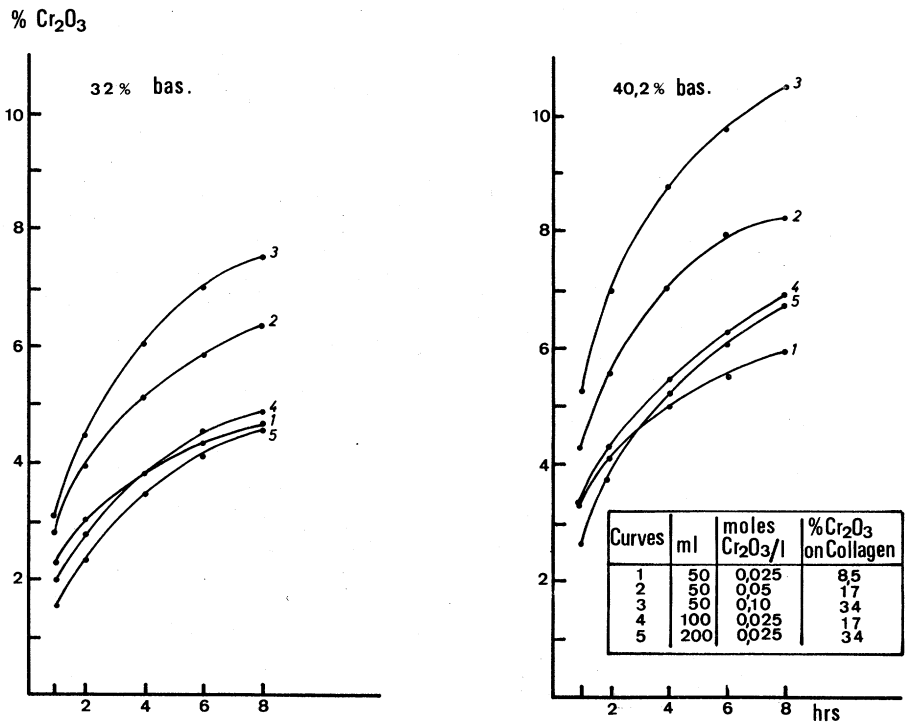

FIGURE 3.—Chrome retention by hide powder. Combined effect of concentration, float ratio, and ratio of chromium to collagen.

the retention of chromium by hide powder from chromium sulfate liquors of 32.0 and 40.2 percent basicity is affected in these two ways. In both cases, the amount of chromium oxide was varied to the same extent from 8.5 percent to 17 percent and 34 percent, respectively. It appears that an increase of the ratio of chromium to collagen at constant volume of the tanning solution, through which the concentration of the solution is also increased (Curves 1, 2, and 3), has a much greater effect on the rate of reaction and on chrome retention than the same increase of this ratio by a proportional increase of the volume of the tanning solution (Curves 1, 4, and 5). Moreover, in this latter case the course of chrome retention at constant basicity depends on the percentage of chromium offered to collagen, as well as on the float ratio. Increasing the float ratio can result both in an increase and in a decrease of chrome fixation. This is regulated by the initial ratio of chromium to collagen and by the tanning time. These phenomena will be discussed in the next section in more detail.

3. THE EFFECT ON CHROME RETENTION OF THE FLOAT RATIO WITH CONSTANT INITIAL CHROME CONCENTRATION

For this study also, portions of 2.5 grams of hide powder were tanned in a total volume of 50, 100, 200, or 400 ml., but now with chrome liquors of equal

initial concentrations. For every basicity of the chrome liquor three series of experiments were carried out, in which the initial concentrations of the tanning solution were 0.125, 0.025, and 0.01 moles Cr_2O_3/l., respectively. Chrome liquors of Series B were used.

Results

For these conditions of tanning, the effect of the float ratio on chromium uptake by hide powder with time appears to be very complicated and to depend on the concentration and on the basicity of the chrome liquor.

At an initial concentration of 0.125 mole Cr_2O_3/l., an increase of the volume of the tanning solution generally causes a decrease of the reaction velocity and

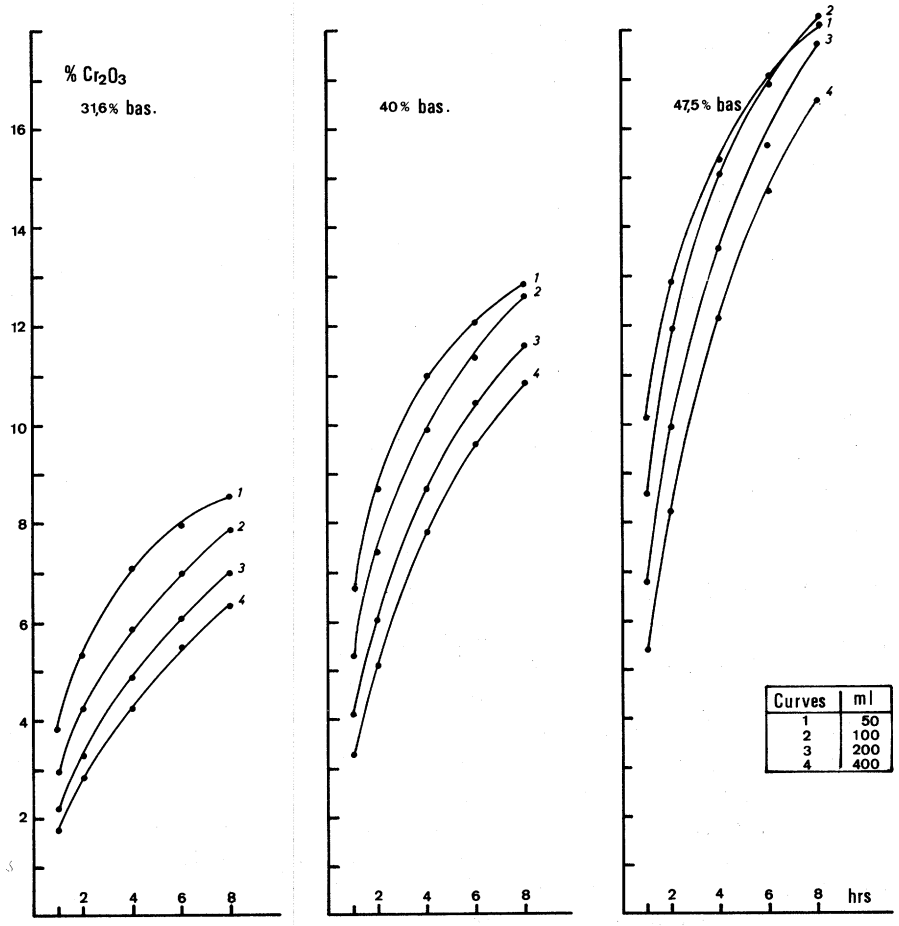

FIGURE 4.—Chrome retention by hide powder. Influence of the volume of chrome liquors having an initial concentration of 0.125 mole Cr_2O_3/l. and different basicities.

of chrome retention (Figure 4), although at higher basicities, and for longer times of tanning only, chrome binding tends to increase first at increasing volumes.

The main effect of varying the volume of chrome liquors with an initial concentration of 0.025 mole Cr_2O_3/l. and with basicities of 31.6 and 40.0 percent (Figure 5) is that the rate of reaction and chromium uptake increase first, followed by a decrease of the same with increase of volume. For chrome liquors of 47.5 percent basicity, however, there is a continuous increase of reaction velocity and chrome retention with increasing volumes of the solution, except for the largest volume in the first hours of tanning.

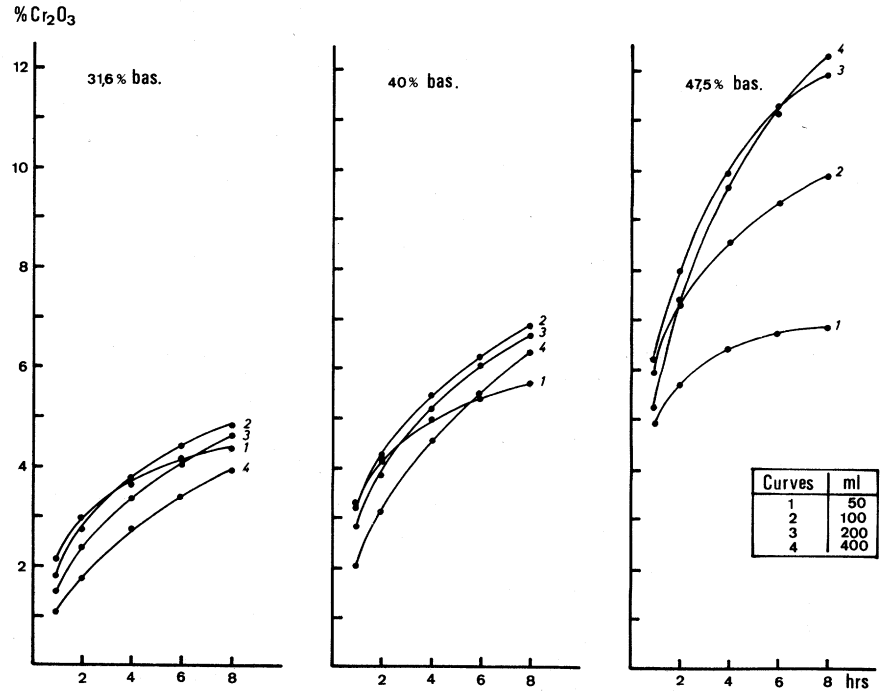

FIGURE 5.—Chrome retention by hide powder. Influence of the volume of chrome liquors having an initial concentration of 0.025 mole Cr_2O_3/l. and different basicities.

Finally, at an initial concentration of 0.01 mole Cr_2O_3/l., an increase of the volume of the tanning liquor also results in the first instance in an increased rate of reaction and chromium uptake (Figure 6). But with a further increase of the volume, the course of chrome retention depends again on the basicity of the chrome liquor. For a basicity of 31.6 percent, chrome retention is slightly retarded when tanning is done in a volume of 400 ml. of the chrome solution, as compared with tanning in a volume of 200 ml. At a basicity of 40 percent, chromium uptake is increased only in the latter stages of tanning, while a further increase

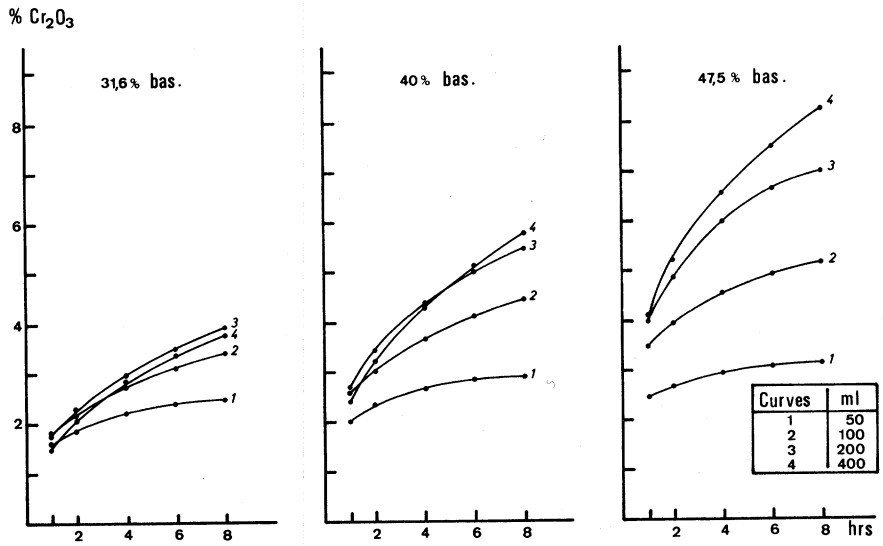

FIGURE 6.—Chrome retention by hide powder. Influence of the volume of chrome liquors having an initial concentration of 0.01 mole Cr_2O_3/l. and different basicities.

of the basicity to 47.5 percent results in an increased chrome retention during the whole period of tanning.

It is obvious that generally the speed of reaction and chrome retention decrease with diminishing initial concentration of the tanning liquor, when all other factors are kept constant.

The pH values of the spent chrome liquors of these tannages are shown in Figure 7. As in the foregoing series, these pH values fall slowly during tanning, after an increase in the first period. For these tanning conditions, the pH level decreases with increasing volumes of the chrome solutions. This decrease of the pH level becomes more pronounced when the chromium concentration also decreases. The pH of tanning is almost constant only when tanning is done with larger volumes of the more concentrated chrome liquors. It is self-evident that the pH level of tannage increases with rising basicity and with decreasing initial concentration of the tanning liquors.

Discussion

The course of the pH of the spent tanning solution as a function of time has already been previously discussed and is attributed to acid binding by collagen and to hydrolysis of the chromium complexes of the tanning liquor. With increasing volume of the same tanning solution, the change in the hydrogen ion concentration due to the removal of acid becomes smaller. The pH level of tannage therefore becomes lower with increasing volume. When tanning is carried

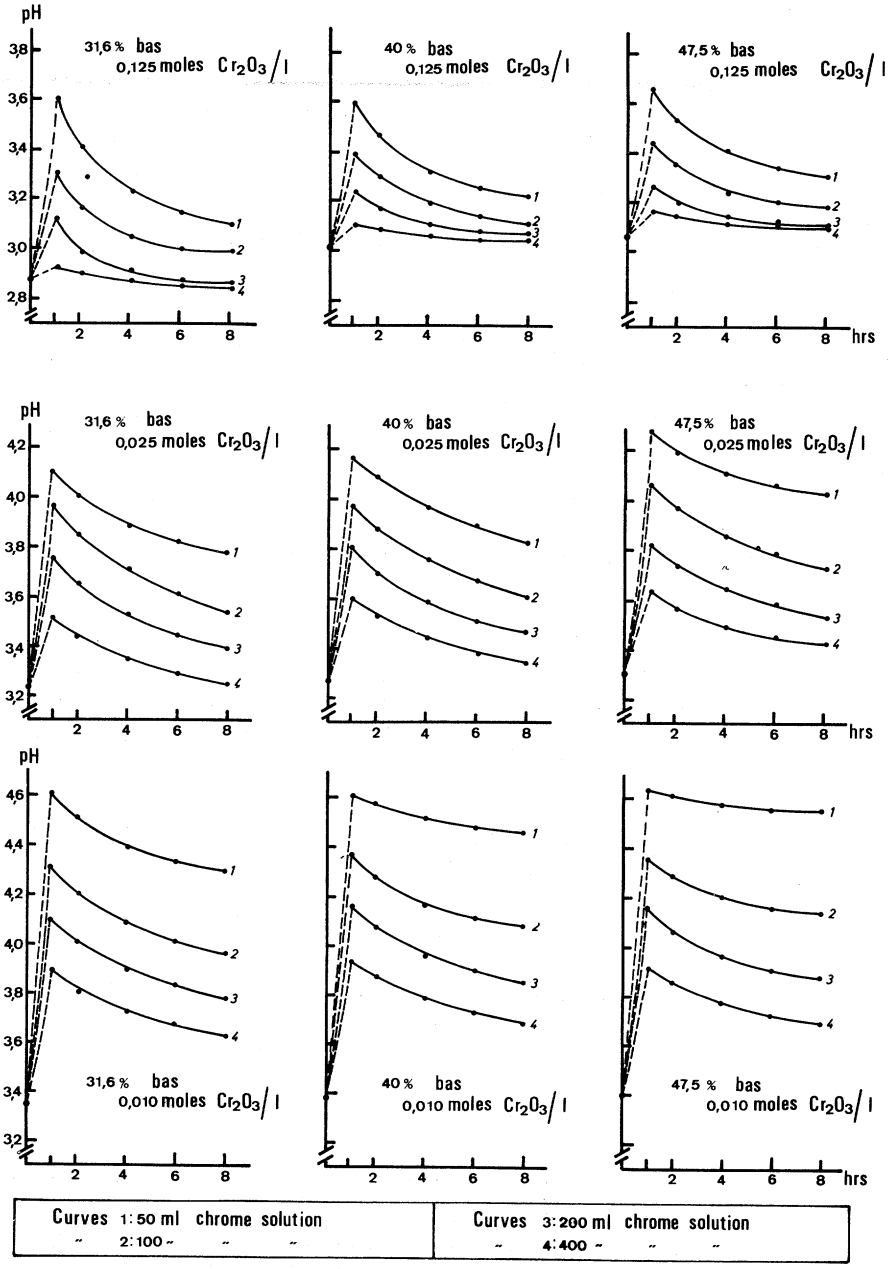

FIGURE 7.—pH values of spent chrome tanning solutions with constant initial chrome concentrations and different volumes and basicities.

out in a larger volume of a more concentrated chrome liquor, the absolute amount of hydrogen ions is comparatively high. Thus the removal of acid by collagen will have a slight influence only on the hydrogen ion concentration, and therefore the pH value of these chrome liquors remains almost constant when tanning proceeds. It appears that these conditions exist when hide powder is tanned at a float ratio of 160:1 with chrome liquors of an initial concentration of 0.125 mole Cr_2O_3/l. (Figure 7, first row, Curve 4).

With decreasing pH level of tanning, the ionization of the carboxyl groups of collagen and the hydrolysis of the chromium complexes in the solution are suppressed. Therefore the affinity of these complexes for collagen and the resulting reaction velocity and chromium uptake will also diminish as the volume of the tanning solution becomes larger. On the other hand, however, it can be expected that the rate of reaction and the retention of chromium will increase with increasing volume of the tanning liquor, owing to a larger ratio of chromium to collagen. Consequently, an increase of the volume of a chrome liquor results, on the one hand, in a decrease of the reaction velocity and of chrome retention due to the decrease of the pH level of tanning, and on the other hand in an increase of the same by a higher ratio of chromium to collagen. It depends on the conditions of tanning, therefore, which of these factors will prevail. Moreover, the basicity of the chrome liquors has also to be considered for an interpretation of the results obtained.

From the experimental results it follows that the effect of a low pH level predominates when hide powder is tanned in various volumes of chrome liquors with an initial concentration of 0.125 mole Cr_2O_3 per liter (Figure 4), irrespective of its basicity. In this case, the rate of reaction, as well as the amount of chromium retained, diminish with increasing volume of the tanning solution. Although a rise of the basicity involves an increased affinity of chromium to collagen, it appears that this greater affinity generally has no influence on the sequence of the curves for chromium uptake with increasing volume, since the pH level of tanning remains low. But especially when tanning is done in a relatively small volume, this greater affinity of the chromium complexes can lead to a more rapid exhaustion of the solution in the first period of tanning and so to some slowing-down of the reaction velocity in the final stage.

In tanning with chrome liquors of initial concentration of 0.025 mole Cr_2O_3 per liter and basicities of 31.6 and 40.0 percent (Figure 5), the pH level also obviously remains so low that the reduced affinity of the chromium complexes for collagen dominates the effect of a larger supply of chromium for larger volumes. In the smallest volume of this chrome liquor, however, the amount of chromium offered to collagen is comparatively low. This leads, after a short space of time, to a rather low concentration of chromium in the solution, and therefore to a distinct fall in the reaction velocity (Figure 5, Curve 1). With rising basicity, the pH level of tanning increases. The counteracting effect of the

pH on chrome fixation therefore becomes gradually smaller and, depending on the other conditions of tanning, a pH level will be reached above which chrome fixation will be promoted, because the ionization of the carboxyl groups of collagen is steadily increasing. Apparently this effect clearly expresses itself in the course of tannages at a basicity of 47.5 percent, for which, as a whole, chrome fixation increases with increasing volume. At fairly low initial concentrations, the pH level of tanning can be so high that no reason exists to assume a counteracting effect of the pH on chrome retention. Consequently, the uptake of chromium by collagen from various volumes of the same chrome liquor will be governed for these cases mainly by the amount of chromium offered to collagen. Hence the reaction velocity and the retention of chromium will increase as the volume of the tanning liquor becomes larger. Generally this appears to be the case when tanning is done with increasing volumes of chrome solutions with an initial concentration of 0.01 mole Cr_2O_3/l. (Figure 6). But for tannages with the greatest float ratio and at a basicity of 31.6 percent (Curve 4), the amount of chromium retained is lower than would be expected for these conditions. Here again the pH level is apparently low enough to dominate to some extent over the increase of chrome retention with increasing volume. This effect of the pH is reduced by the increasing affinity between the chromium complexes and collagen with rising basicity. This influence of the basicity is evident, because the curves for chromium uptake by hide powder tanned at the greatest volume ratio (Curve 4) shift gradually to a higher chrome fixation in a given space of time with increasing basicity, as compared with the curves for tannages at lower float ratios.

CONCLUSION

From the results obtained, the general conclusion can be drawn that the influence of the float ratio on the rate of chrome retention by hide powder tanned in chromium sulfate liquors is interrelated in a rather complicated way with the initial concentration and the basicity of the tanning solution. Especially in the event of tanning with various volumes of chrome liquors of equal initial concentration, the possibility of finding an increased, a decreased, or even an increased followed by a decreased, rate of reaction and chrome fixation for increasing float ratios depends in the first instance on the concentration level of the tanning solutions. Particularly when tanning is done with chrome liquors of fairly low initial concentration, the basicity of the chrome liquor is also important in this respect.

REFERENCES

1. Briggs, P. S. *J. Soc. Leather Trades' Chemists,* **29,** 123 (1945); **30,** 189 (1946); **31,** 86 (1947); **32,** 56 (1948); **34,** 165 (1950); **35,** 57 (1951); **50,** 139 (1966).
2. de Wijs, J. C. *J. Soc. Leather Trades' Chemists,* **45,** 242 (1961).
3. Otto, G. Thesis, Karlsruhe, 1928, cited in References 4 and 5.

4. Gustavson, K. H. "The Chemistry of Tanning Processes," p. 99–101, Academic Press, New York, 1956.

5. Gustavson, K. H. "Handbuch der Gerbereichemie," Vol. II/2, p. 255–257, (Grassmann, W., Editor), Vienna, 1939.

6. Internat. Comm. Chem. Anal. Leather. *J. Soc. Leather Trades' Chemists,* **49**, 17 (1965).